

The former existence of cold in what are now warm latitudes might, and probably did in part, arise from other causes than a change in the axis of rotation, but no other hypothesis can well account for the existence of traces of an almost tropical vegetation within the Arctic circle.

Of the former existence of such a vegetation, the evidence, though strong, is not conclusive. But if the fossil plants of Melville Island, in lat. 75° N.*, which appear to agree generically with those from the English coal-measures, really grew upon the spot where they were now discovered, they seem to afford conclusive evidence of a change in the position of the pole since the period at which they grew, as such vegetation must be considered impossible in so high a latitude.

The corals and Orthoceratites from Griffiths Island and Cornwallis Island, and the liassic Ammonites from Point Wilkié, Prince Patrick's Island, tell the same story of the former existence of something like a sub-tropical climate at places at present well within the Arctic circle.

To use the words of the Rev. Samuel Haughton†, in describing the fossils collected by Sir F. L. McClintock, "The discovery of such fossils *in situ*, in 76° N. latitude, is calculated to throw considerable doubt upon the theories of climate, which would account for all past changes of temperature by changes in the relative position of land and water on the earth's surface;" and I think that all geologists will agree with this remark, and feel that if the possibility of a change in the position of the axis of rotation of the crust of the earth were once admitted, it would smooth over many difficulties they now encounter.

That some such change is indeed taking place at the present moment may not unreasonably be inferred from the observations of the Astronomer Royal, who, in his Report to the Board of Visitors for 1861, makes use of the following language, though "only for the sake of embodying his description of the observed facts," as he refers the discrepancies noticed to "some peculiarity of the instrument. . . . The Transit Circle and Collimators still present those appearances of agreement between themselves and of change with respect to the stars which seem explicable only on one of two suppositions—that the ground itself shifts with respect to the general Earth, or that the Axis of Rotation changes its position."

March 22, 1866.

Lieut.-General SABINE, President, in the Chair.

The following communications were read:—

* Lyell, 'Principles of Geology,' 1853, p. 88.

† Journal of the Royal Dublin Society, vol. i. p. 244.

- I. "On the Action of Trichloride of Phosphorus on the Salts of the Aromatic Monamines." By A. W. HOFMANN, LL.D., F.R.S., &c. Received March 3, 1866.

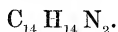
The starting-point of the following experiments was an accidental observation. Whilst investigating the chlorine-, bromine-, and nitro-derivatives of aniline, I had prepared a large quantity of phenylacetamide by the action of chloride of acetyl on aniline. From the hydrochlorate of aniline, abundantly produced as a by-product in this reaction, the aniline was recovered by treating the mother-liquors with hydrate of sodium. During the distillation, after the greater part of the aniline had passed over and collected in the receiver, a tenacious oily fluid began to come over, adhering to the tube of the condenser and gradually becoming a crystalline mass. It was easily purified by washing with cold, and crystallization from hot alcohol.

Beautiful white leafy crystals were thus obtained, fusible at 137° , and volatile without decomposition at a temperature beyond the range of the mercury-thermometer. These crystals are almost insoluble in water, difficultly soluble in cold, but soluble in hot alcohol, and also soluble in ether. The solutions are neutral.

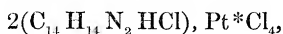
In acids the crystals are also easily soluble; an alkali precipitates the original substance unaltered from the solutions. The hydrochloric-acid solution yields, with tetrachloride of platinum, a difficultly soluble crystalline precipitate. The new substance thus exhibits the deportment of a well-characterized base. Its composition was readily determined by combustion with oxide of copper, the analytical results pointing unequivocally to the formula



as the simplest atomic expression for the new body. But the whole behaviour of the substance, and more especially its transformation, by means of concentrated sulphuric acid, into aniline and acetic acid, leave no doubt that the above expression must be doubled, and that the new base is represented by the formula



This formula was confirmed by the analysis of the platinum-salt already mentioned, and that of the nitrate which separates from the solution as an oily fluid, gradually changing to a beautiful crystalline compound; the former contains



the latter

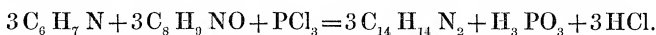


Whence is this body derived? and how is its formula to be interpreted? An answer to these questions was furnished by examining the chloride of acetyl employed in preparing the phenylacetamide. When on distilling the chloride the principal product had passed over, the thermometer gra-

* Pt=198.

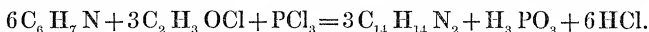
dually rose from 55° to 78°. The last portion which came over was pure trichloride of phosphorus. It was obvious that this substance must have played a part in the formation of the new compound.

I therefore submitted phenylacetamide to the action of trichloride of phosphorus. The new body was formed, but in very unsatisfactory quantity. The result of the experiment was essentially different when phenylacetamide and aniline in varying proportions were jointly submitted to the action of trichloride of phosphorus. The amount of substance obtained varied with the composition of the mixture, and appeared greatest when the mixture was made in the proportion of one part of trichloride of phosphorus, two parts of aniline, and three parts of phenylacetamide. Hence the reaction had taken place according to the following equation :

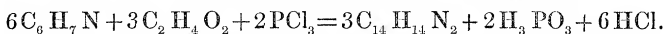


Perfectly similar results were obtained when a proportionate quantity of hydrochlorate of aniline was employed instead of aniline in this experiment.

The idea naturally presented itself to produce the same result without taking the trouble of preparing and purifying the phenylacetamide by including its preparation in the very process of forming the new compound. For this purpose 6 molecules of aniline were added to 3 molecules of chloride of acetyl, and the dense liquid thus obtained mixed with 1 molecule of trichloride of phosphorus. The result could not have been better :



A simple additional step and the true mode of preparing the substance, and with it the general method for the production of an endless variety of analogous bodies, was found. Evidently it was not even necessary to prepare the chloride of acetyl separately. The new body must be as easily obtained by the direct action of trichloride of phosphorus on aniline and acetic acid. The mixture had only to be made in such a manner that, after transforming the acetic acid into chloride of acetyl, there was a sufficient amount of trichloride of phosphorus left to perform the rest of the work. In this case, therefore, 6 molecules of aniline and 3 molecules of acetic acid had to be added to 2 molecules of trichloride of phosphorus,

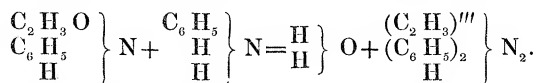


The reaction is violent, and the operation must be performed with care. The substances are mixed according to the above equation. For this purpose three parts by weight of aniline are added to one part of acetic acid and into the mixture surrounded by cold water two parts of trichloride of phosphorus are slowly poured ; in which proportion the latter compound is in slight excess. The tenacious fluid thus obtained is then heated for a couple of hours to 160°. On cooling, it solidifies to a hard, friable, translucent, resinous mass of a light-brown colour, which dissolves in boiling water almost without residue, leaving only traces of an amorphous yellow

substance containing phosphorus behind. The clear filtered solution, after cooling, yields, on the addition of soda, a white crystalline precipitate, which requires only to be washed and recrystallized from alcohol.

The foregoing equations give a pretty clear idea of the qualitative and quantitative nature of the experiment, but they do not afford us an insight into the true mechanism of the reaction. This, nevertheless, is a very simple one. Trichloride of phosphorus acts water-generating and water-withdrawing. The oxygen required for this purpose is supplied by the phenylacetamide; as, however, the molecule of this compound contains but one atom of hydrogen belonging to the original ammonia skeleton, a molecule of aniline is required in addition to supply the second atom of hydrogen. In this manner a diamine is formed, in which two atoms of the hydrogen of the double ammonia type are replaced by two univalent phenyl-residues, and three of the remaining hydrogen atoms by the trivalent group C_2H_3 , to which the term *ethenyl** may for the present be applied.

The new body would thus become *ethenyldiphenyldiamine*, the formation of which in the most simple form would depend upon the removal of 1 mol. of water from 1 mol. of phenylacetamide and 1 mol. of aniline.



I was anxious to test this assumption by experiment.

* The term *ethenyl* proposed for the group C_2H_3 , which in the new compound functions with the value of 3 atoms of hydrogen, is framed according to a system of nomenclature to which I have occasionally resorted, in the boundless confusion of names now prevailing in organic chemistry, as a means of communication with my pupils. Perhaps this system is capable of further development.

It is a peculiar feature of the development of modern chemistry that more than ever before is felt the necessity of grouping the organic compounds round the hydrocarbons. The question therefore may be said to reduce itself to the discovery of a good principle of nomenclature for the compounds of hydrogen and carbon. Many attempts have been made in this direction, as yet without any acceptable results.

For the purpose of framing my names I fuse the method originally employed by Laurent with the principle proposed by Gerhardt, and more or less adopted by his successors.

An example will illustrate my mode of proceeding. Let us consider the most important of all the series of hydrocarbons, the homologues of marsh-gas. All the members of this series I make terminate in *ane*, distinguishing the order of succession by prefixing the first syllable of the Latin numeral corresponding to the number of carbon atoms in the molecule. From this rule the first three members of the series are conveniently excepted, their names having been so long in use as to render it desirable to embody them in the system.

By the removal of 1 atom of hydrogen from the hydrocarbon, the latter ceases to be a *saturated* compound, and the remaining group of atoms becomes *univalent*. The termination *yl* now takes the place of *ane*. A second atom of hydrogen is removed, the group becomes *bivalent* and now terminates in *ene*; a third hydrogen atom is separated, the group is again raised in value by one becoming in fact *trivalent*, and acquires the termination *enyl*. By the removal of the fourth and fifth atom of hydrogen the

At 100° iodide of ethyl has no action on ethenyldiphenyldiamine, but at about 150° the two bodies react on one another. The mixture, after being heated for five or six hours, yielded, upon cooling, beautiful crystals of an iodide. By treatment with chloride of silver this iodide was converted into the corresponding chloride, and then into the platinum-salt. Analysis of this salt showed that the ethyl group had been once taken up. On the addition of caustic soda the corresponding base was separated. It is a thick oily fluid, which, when shaken with water, *does not impart to it the slightest alkaline reaction*. By renewed treatment with iodide of ethyl an iodide, it is true, was separated, but it was proved on examination that the ethyl group had not been assimilated a second time. In the sense of the above assumption, this nevertheless ought to have taken place. The experiment was therefore repeated with iodide of methyl which is well known to act much more powerfully than the ethyl-compound. This body attacks the ethylated base even at 100°. The iodide thus obtained, when decomposed by oxide of silver, yielded a *strongly alkaline liquid*, whence

quantivalence of the residuary group again increases, the groups becoming *quadri-valent* and *quintivalent*, and acquiring the terminations *ine* and *inyl*, &c.

According to this principle the following names are formed :

Methane, (C H ₄) ⁰	Sextane, (C ₆ H ₁₄) ⁰
Ethane, (C ₂ H ₆) ⁰	Septane, (C ₇ H ₁₆) ⁰
Propane, (C ₃ H ₈) ⁰	Octane, (C ₈ H ₁₈) ⁰
Quartane, (C ₄ H ₁₀) ⁰	Nonane, (C ₉ H ₂₀) ⁰
Quintane, (C ₅ H ₁₂) ⁰	Decane, (C ₁₀ H ₂₂) ⁰

And further :

Methane, (C H ₄) ⁰	Ethane, (C ₂ H ₆) ⁰	Propane, (C ₃ H ₈) ⁰	Quartane, (C ₄ H ₁₀) ⁰
Methyl, (C H ₃) ⁱ	Ethyl, (C ₂ H ₅) ⁱ	Propyl, (C ₃ H ₇) ⁱ	Quartyl, (C ₄ H ₉) ⁱ
Methene, (C H ₂) ⁱⁱ	Ethene, (C ₂ H ₄) ⁱⁱ	Propene, (C ₃ H ₆) ⁱⁱ	Quartene, (C ₄ H ₈) ⁱⁱ
Methenyl, (C H) ⁱⁱⁱ	Ethenyl, (C ₂ H ₃) ⁱⁱⁱ	Propenyl, (C ₃ H ₅) ⁱⁱⁱ	Quartenyl, (C ₄ H ₇) ⁱⁱⁱ
	Ethine, (C ₂ H ₂) ^{iv}	Propine, (C ₃ H ₄) ^{iv}	Quartine, (C ₄ H ₆) ^{iv}
	Ethinyl, (C ₂ H) ^v	Propinyl, (C ₃ H ₃) ^v	Quartiny, (C ₄ H ₅) ^v
		Propone, (C ₃ H ₂) ^{vi}	Quartone, (C ₄ H ₄) ^{vi}
		Proponyl, (C ₃ H) ^{vii}	Quartonyl, (C ₄ H ₃) ^{vii}
			Quartune, (C ₄ H ₂) ^{viii}
			Quartunyl, (C ₄ H) ^{ix}

This is not the place to develop this subject further. The short notice I have given must suffice. A superficial examination of the system shows, however, how large a number of groups of atoms may be clearly and succinctly expressed in it.

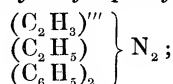
It appeared convenient to submit the plan to a provisional test by framing some of the names required for the substances which were furnished by the above experiments.

Bodies containing oxygen may be as simply nominated according to this plan.

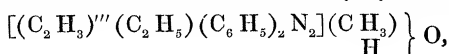
The acid derived from *ethylic alcohol* is *ethoxylic acid* (acetic acid), the first acid corresponding to *ethenic alcohol* would be *ethoxenic acid* (glycolic acid), the second being *ethdiozenic acid* (oxalic acid). We speak of the *oxylic*, *oxenic*, and *dioxenic acids* of a series, of the *quartane series*, for instance, and any one would understand that by these expressions are meant butyric, butylactic, and succinic acids.

it was at once inferred that the methyl group had been added to the ethyl group already present in the substance. This conclusion was amply corroborated by the analysis of the platinum-salt precipitated from the liquid.

By this experiment the nature of ethenyldiphenyldiamine is most satisfactorily elucidated. The action of iodide of ethyl had converted this base into the tertiary diamine *ethenylethyldiphenyldiamine*,

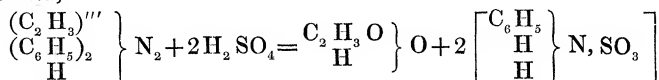


the latter, under the influence of iodide of methyl, yielding the compound



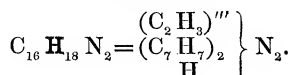
which is soluble in water with a strongly-marked alkaline reaction.

The stability of ethenyldiphenyldiamine is remarkable. As I have already mentioned, this base distils at a very high temperature without decomposition. It is moreover scarcely attacked by fusion with hydrate of potassium. Concentrated sulphuric acid, on the other hand, decomposes it easily. When gently heated, the solution of ethenyldiphenyldiamine in sulphuric acid evolves acetic acid, and, on addition of water, the slightly-coloured liquid solidifies to a white crystalline mass of *sulphanilic acid*,

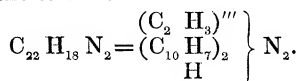


It need scarcely be mentioned that, by reactions similar to that of trichloride of phosphorus on acetate of aniline, an almost endless variety of new compounds may be obtained. By changing the acid, or base, or both, a series of substances is formed, the composition of which in each case is fixed in advance by theory. I have worked only very little in this direction.

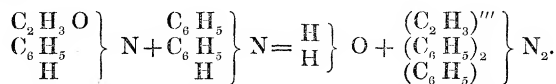
Toluidine acts in a manner precisely similar to that of aniline. The base formed can scarcely be distinguished from the phenyl base. Analysis of the platinum-salt has led to the formula



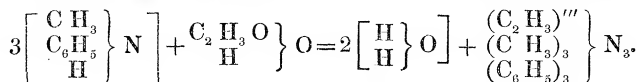
With *naphthylamine* the reaction is less smooth. The product obtained by acting with 1 molecule of trichloride of phosphorus on 3 molecules of chloride of acetyl and 6 molecules of naphthylamine, was an unenjoyably viscous scarcely crystalline mass which retained, after repeated solution and precipitation, its amorphous character. An analysis of the platinum-salt led, however, to the formula



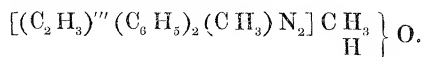
Aniline, toluidine, and naphthylamine being *primary* monamines, it seemed of interest also to extend the examination to a *secondary* one. For this purpose I selected *diphenylamine*. When a mixture of diphenylamine and phenylacetamide, in the proportion of their molecular weights, was submitted to the action of trichloride of phosphorus, the reaction took place in the ordinary way, but the mass precipitated from the solution of the chloride by ammonia could not be crystallized. It had therefore to be analyzed as platinum-salt. Determination of the platinum as well as combustion showed, however, that the expected *ethenyltriphenyldiamine* had been formed,



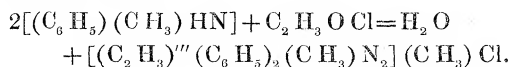
An entirely unexpected result, on the other hand, was obtained by the action of trichloride of phosphorus on a mixture of acetic acid and *methylaniline*. Working, as I did, exclusively with a secondary monamine, I had expected to see the reaction take place according to the following equation:—



But this was not the case; the action was found to have been very irregular; and amongst the products a chloride was observed, the base of which, when liberated by oxide of silver, dissolved in water *with an alkaline reaction*. When analyzed in the form of a platinum-salt, this body proved to be ethenyldiphenyldiamine, which had twice appropriated the methyl-group, having the composition



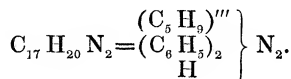
In this case evidently chloride of methyl had been eliminated from one of the molecules of methylaniline, which, acting on the ethenyldiphenylmethyldiamine, had given rise to the formation of the chloride corresponding to the above-mentioned oxide,



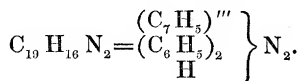
A few experiments made with the derivatives of valeric and benzoic acids are still to be mentioned.

Quintenyldiphenyldiamine.—For the preparation of this substance, 3 molecules of valeric acid were mixed with 6 molecules of aniline, and to the liquid, after cooling, 2 molecules of trichloride of phosphorus were added. This mixture, on being submitted for a couple of hours to a temperature of 150°, yielded a viscous mass soluble in water. From the solution hydrate of sodium precipitated a crystalline base almost insoluble in water, which was recrystallized from alcohol. This substance fused at 111°. The com-

bustion of the body and the analysis of its platinum-salt, which crystallized in rhombic plates difficultly soluble in water and almost insoluble in alcohol, led to the formula

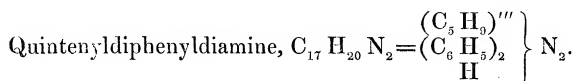
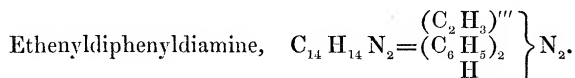
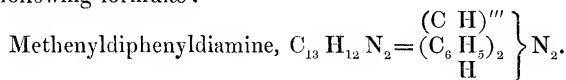


Benzylidiphenyldiamine.—By substituting benzoic acid for valeric acid in the reaction just described, the corresponding benzyl-compound is obtained. I have prepared this substance by the action of 1 molecule of trichloride of phosphorus on a mixture of 3 molecules of phenylbenzamide and 3 molecules of hydrochlorate of aniline. The reaction takes place in the ordinary way. The product is a very weak base crystallizing in fine silky needles. The hydrochlorate forms thin brilliant plates difficultly soluble in water, which upon re-crystallization lose their acid. The analysis led to the formula



This compound has been already observed by Gerhardt. He obtained it whilst examining the action of pentachloride of phosphorus on the amides, the last experiments which he performed before his death. A short notice of this investigation, found after his death, has been published by M. Cahours*.

The phenyl-compounds of the acetic and valeric groups above described are naturally linked with a compound which several years ago I procured by an essentially different reaction. This substance, which at the time I described under the name of *formyldiphenyldiamine*†, but to which, in accordance with my present ideas on nomenclature, I would give the name *methenyldiphenyldiamine*, is obtained by the action of chloroform on aniline; its relation to the compounds before mentioned is seen by a glance at the following formulæ:—



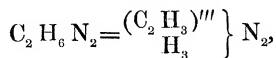
It seemed worth while to establish by a special experiment the analogy of methenyldiphenyldiamine, obtained in so different a reaction, with the substances just described. For this purpose I submitted *phenylform-*

* Ann. Ch. Phys. [3], vol. liii. p. 302.

† Proceedings of the Royal Society, vol. ix. p. 229.

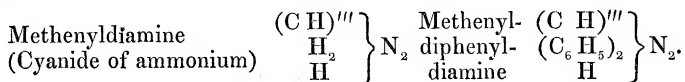
*amide** to the action of a mixture of aniline and trichloride of phosphorus. The result proved that the methenyl-compound can be thus prepared even more easily than by means of chloroform.

In conclusion, the relation must be mentioned which the compounds just described bear to the base obtained by Professor Strecker †, when acting with gaseous hydrochloric acid on acetamide. The body thus formed is



and has been called *acediamine*, for which name, in accordance with the proposed nomenclature, I would now substitute the term *ethenyldiamine*. When compared with the analogous aniline-compound, the very slight stability of acediamine, which splits up with the greatest facility into acetic acid and ammonia, deserves to be noticed.

A *quintenyldiamine*, corresponding to the quintenyldiphenyldiamine, has not as yet been prepared. Methenyldiamine, on the other hand, is known, although the compound which I have in view has scarcely been looked upon as such. The body in question is no other than *cyanide of ammonium*.

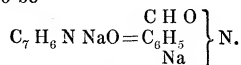


The facility with which this substance decomposes is well known; amongst the products *formic acid* and *ammonia* are invariably found.

It is further known that by heating ammonia with chloroform (trichloride of methenyl), cyanide of ammonium is formed, a reaction which is perfectly similar to that by which the analogous phenyl-base was originally obtained in the corresponding experiment with aniline.

In conclusion, I beg to thank Messrs. Tingle and Fischer for their valuable assistance during the performance of the experiments described.

* On this occasion I prepared larger quantities of phenylformamide, which can be produced much more easily by digesting formic ether with aniline than by the process hitherto employed (distillation of oxalate of aniline). Phenylformamide has the remarkable property (not as yet observed) of being precipitated from its aqueous solution as a solid scarcely crystalline mass on addition of a strong solution of caustic soda. By separating this compound from the liquid, and purifying it as far as possible by rapid pressure between folds of bibulous paper, it was possible to make an analysis of it. Its composition was found to be



By the action of water upon it phenylformamide and hydrate of sodium are reproduced.

† Ann. Chem. Pharm., vol. ciii. p. 321.